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(54) Title: SOLID DETERGENT COMPOSITIONS

## (57) Abstract

The present invention relates to solid detergent compositions or components thereof containing a cationic surfactant, which contains at least one cationically charged quaternary amine group and at least one primary, secondary or tertiary amine group, and additional ingredients. The compositions or components of the invention are particularly useful in laundry and dish washing processes to provide enhanced greasy stain removal and good dispensing and/or dissolution.

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## Solid Detergent Compositions

### Technical Field

The present invention relates to solid detergent compositions or components thereof containing a cationic surfactant, which contains at least one cationically charged quaternary amine group and at least one primary, secondary or tertiary amine group, and additional ingredients. The compositions or components of the invention are particularly useful in laundry and dish washing processes to provide enhanced greasy stain removal and good dispensing and/ or dissolution.

### Background to the Invention

It is known to use cationic surfactants in detergent compositions. For example, GB 2040990A describes granular detergent compositions comprising cationic surfactants. Cationic surfactants are also described in combination with anionic surfactants, for example in EP-A-0 121 949.

The Applicants have found that certain cationic surfactants, or polyamine cationic surfactants, containing at least one cationically charged quaternary amine group and at least one primary, secondary or tertiary amine group are very good surfactants, suitable for use in cleaning or detergent compositions. These compounds are found to be very surface active under alkaline washing conditions, and they are found to give excellent cleaning performance benefits. This is believed to be due to the compounds containing both a positively charged group and a neutral, more hydrophobic group.

Furthermore, several examples of these surfactants are found to be more biodegradable and to have a very low aquatic toxicity, relative to most quaternary amine compounds.

It has been found that the stability of the polyamine cationic surfactants is not affected by changes of the pH. Furthermore, it has been found that, depending on their structure, most of the polyamine cationic compounds of the present invention

and detergent compositions containing these polyamine cationic surfactants, are stable under standard storage and washing conditions.

The Applicant has furthermore found that the use of these polyamine cationic surfactants in solid detergents provides improved dispensing (via the drawer of washing machine or via a dosing device inside the washing machine), dispersion through the wash and even dissolution in the wash water. Gelling problems which occur using conventional detergent compositions in particular those which contain the cationic surfactants, are reduced for both high and low density detergent compositions. Without wishing to be bound by theory, the Applicant believes that this is because the particular cationic surfactants used in the detergent compositions of the present invention have surprisingly good solubility and form an association in the presence of anionic components to produce surprisingly soluble anionic/cationic complexes, which leads to good dispensing and dispersion of the solid compositions or components thereof.

Furthermore, the Applicants have found that the incorporation of these cationic surfactants in solid detergent compositions or components thereof, also improves the easy of formulation of these compositions or components. It has been found that when the process for making the compositions or components involves the step of formation of a slurry, the viscosity of the slurry can be reduced by incorporation of these cationic surfactants. Thus, the flowability of the composition or component or the slurry can be improved.

All documents cited in the present description are incorporated herein by reference.

#### Summary of the invention

The present invention provides a solid detergent composition or component comprising:

- (a) at least 0.01% by weight of the composition or the component thereof, one or more cationic surfactants, comprising at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group.

- (b) from 0.1% to 99.99% by weight of the composition or the component thereof, additional detergent ingredients.

It can be preferred that the solid composition or component thereof, is a compact or concentrated composition or component thereof, having a bulk density of 570gr/l or more.

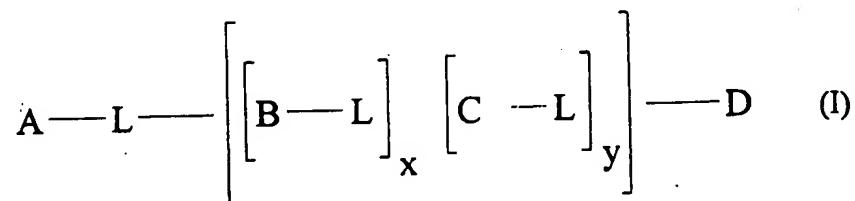
The invention also relates to the use of a at least 0.01%, preferably at least 0.05%, more preferably at least 0.3% by weight of one or more cationic surfactants, comprising at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group, in a solid detergent composition for improving the dispensing and/ or dispersion or the dissolution of the composition into the wash water.

#### Detailed description of the invention

##### Cationic surfactant

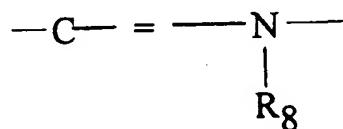
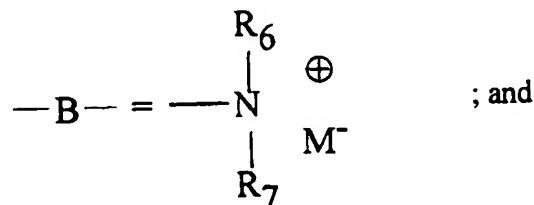
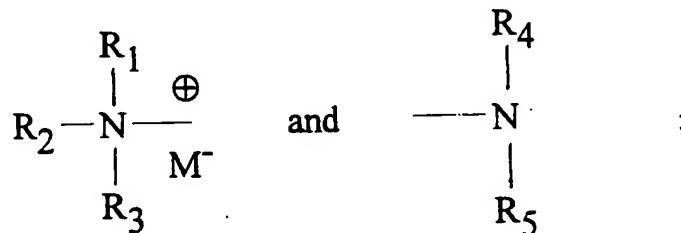
The compositions or components of the invention comprise at least 0.01% by weight of the composition or the component thereof, a cationic surfactant, which contains at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group.

Preferred cationic surfactant of the present invention are polyamine cationic surfactants of the general formula (I):



wherein L is a linking unit, and each L is independently selected from the group consisting of C<sub>2</sub>-C<sub>30</sub> linear or branched alkylene, alkenylene, alkarylene, aralkylene,

arylene, (poly) hydroxyalkylene, (poly) alkylenoxy, (poly) hydroxy alkenylene; L can be substituted by one or more A, B, C or D units; x is a number from 0 to 10, y is a number from 0 to 10; and wherein the units A- and D- are each independently selected from



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are independently selected from the group consisting of C<sub>1</sub>-C<sub>30</sub> linear or branched alkyl, alkenyl, alkaryl, aralkyl, aryl, (poly) hydroxyalkyl, (poly) hydroxy alkenyl, alkoxy group and hydrogen, one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> or R<sub>8</sub> can be a linear or branched polyoxyalkylene group with from 2 to 26 oxyalkylene units or R<sub>1</sub> and R<sub>2</sub>, R<sub>1</sub> and R<sub>2</sub> and R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> or R<sub>6</sub> and R<sub>7</sub> form together with the nitrogen atom part of a ring structure; or R<sub>3</sub> is not present and R<sub>1</sub> or R<sub>2</sub> is double bonded to the nitrogen; or R<sub>7</sub> is not present and R<sub>6</sub> is double bonded to the nitrogen; or R<sub>5</sub> is not present and R<sub>4</sub> is double bonded to the nitrogen; or, when x and y are 0, R<sub>1</sub> or R<sub>2</sub> or R<sub>3</sub> and R<sub>4</sub> or R<sub>5</sub> form together with the nitrogen atoms of A and D part of a ring structure; M<sup>-</sup> is one or more counterions, and at least one A or D comprises a quaternized ammonium group in which none of R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> is hydrogen, or at least one B is present in which neither R<sub>6</sub> nor R<sub>7</sub> is hydrogen, and at least one A or D comprises a primary, secondary or tertiary amine group, or at least one C is present.

The units B-L and C-L are linked when both are present (i.e. when x and y do not equal 0), and they can be randomly present along the chain between the end units A-L and D.

Preferably, the value of x+y is from 1 to 4. Preferably, when x+y is greater than 1, at least one of present groups A, B, C or D is a secondary or primary ammonium group.

More preferably, x=0 and y is a number from 1 to 4. Even more preferably, both x and y are 0.

If x+y does not equal 0, it is preferred that the surfactant comprises only one quaternary group A or D.

Preferably R<sub>6</sub>, R<sub>7</sub> and/or R<sub>8</sub> are each independently selected from a C<sub>1</sub>-C<sub>6</sub>, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl, alkoxyalkyl or (poly) hydroxyalkyl group or, most preferably hydrogen.

Preferably, R<sub>1</sub> is a C<sub>6</sub>-C<sub>14</sub> alkyl, (poly) hydroxyalkyl or alkoxy group or an aralkyl group, most preferably a 2-ethylhexyl group, R<sub>2</sub> and R<sub>3</sub> are each independently C<sub>1</sub>-C<sub>6</sub>, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl or hydroxyalkyl groups and preferably R<sub>4</sub> and R<sub>5</sub> (and R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> when present) are each independently C<sub>1</sub>-C<sub>6</sub>, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl, alkoxyalkyl or (poly) hydroxyalkyl groups or, most preferably, hydrogen atoms.

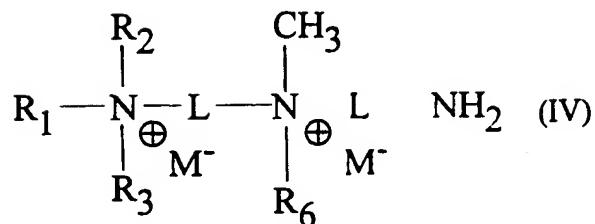
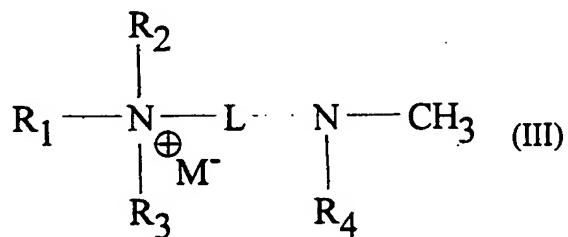
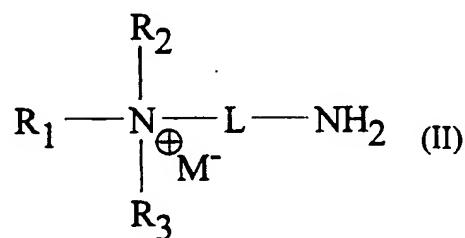
In a further preferred alternative, R<sub>4</sub> is preferably a C<sub>6</sub>-C<sub>14</sub> alkyl, (poly) hydroxyalkyl, alkoxy group or an aralkyl group, most preferably a 2-ethylhexyl group R<sub>5</sub> is preferably a C<sub>1</sub>-C<sub>6</sub>, more preferably a C<sub>1</sub>-C<sub>3</sub> alkyl, (poly) hydroxyalkyl group or hydrogen and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> (and R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> when present) are each independently preferably C<sub>1</sub>-C<sub>6</sub>, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl, alkoxyalkyl or (poly) hydroxyalkyl groups or aralkyl groups.

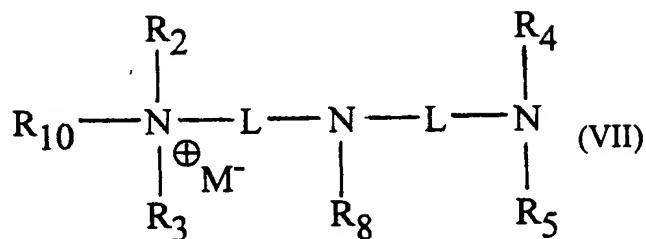
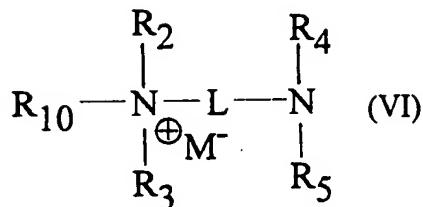
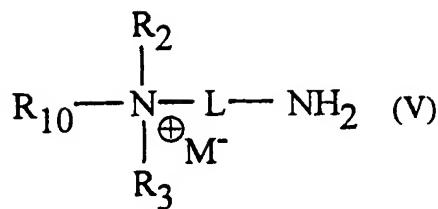
When R<sub>1</sub> and R<sub>2</sub>, R<sub>1</sub> and R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> or R<sub>6</sub> and R<sub>7</sub> form together with the nitrogen atom part of a ring structure, the ring structure is preferably a benzene ring structure, morpholino ring structure or a piperazino ring structure, or a substituted benzene or substituted morpholino or substituted piperazino ring structure.

When  $x+y$  is 0 and  $R_1$  or  $R_2$  or  $R_3$  and  $R_4$  or  $R_5$  form together with the nitrogen atoms of group A and D part of a ring structure, the ring structure is preferably a benzene ring structure, morpholino ring structure or a piperazino ring structure, or a substituted benzene or substituted morpholino or substituted piperazino ring structure.

$L$  groups are independently preferably a  $C_2$ - $C_8$ , more preferably a  $C_2$ - $C_4$  linear or branched alkyl, hydroxy alkyl, alkoxy or hydroxy alkoxy group. If  $x+y$  is 0, the  $L$  group is preferably a  $C_2$  alkyl group. If group  $L$  comprises more than 2 carbon atoms, the surfactant preferably comprises at least one primary or secondary A, B, C or D group.

Examples of preferred polyamine cationic surfactants of the present invention are:

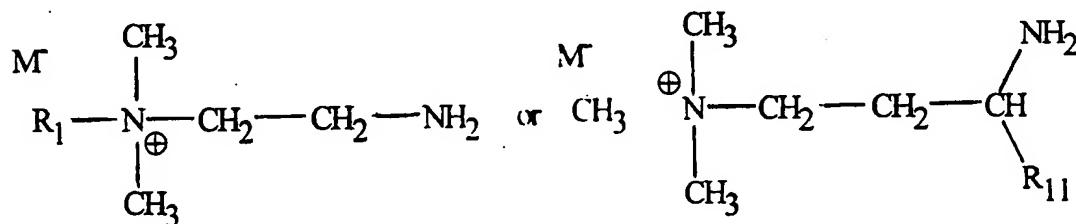




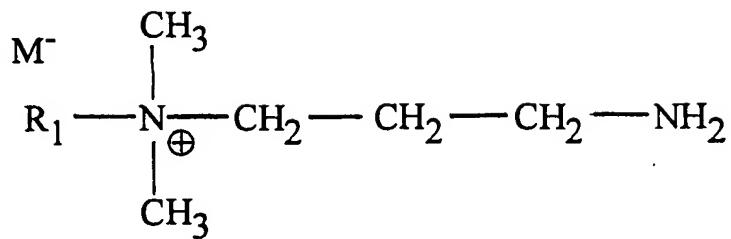
wherein  $\text{R}_1$ ,  $\text{R}_4$ ,  $\text{R}_6$  and  $\text{R}_8$  are as described above;  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_5$  are independently selected from the group consisting of methyl, ethyl, hydroxyethyl, hydroxypropyl, polyhydroxy propyl, ethoxy, propoxy or 2,3,4,5,6-penta hydroxy hexyl, and are most preferably methyl or hydroxyethyl groups;  $\text{R}_{10}$  is a methyl or hydroxyethyl group;  $\text{L}$  is as described above;  $\text{R}_1$  and/or  $\text{R}_2$  and/or  $\text{R}_4$  are most preferably a 2-ethylhexyl group.

A highly preferred cationic polyamine surfactant is of formula VI, as defined above, wherein  $\text{R}_2$  is a hydroxypropyl or hydroxyethyl group,  $\text{R}_3$  and  $\text{R}_{10}$  are methyl groups,  $\text{L}$  is  $\text{C}_2\text{-C}_3$  alkyl group.

Highly preferred polyamine cationic surfactant are those of the formulas:



or



wherein  $\text{R}_1$  is as described above, preferably a  $\text{C}_2\text{-C}_{14}$ , preferably  $\text{C}_6\text{-C}_{14}$  linear or branched alkyl, (poly) hydroxy alkyl, alkoxy or aralkyl group; particularly preferred  $\text{R}_1$  groups are hydroxyalkyl groups, where the alkyl groups have 2 to 5 carbon atoms, especially hydroxyethyl and hydroxypropyl are preferred; particularly preferred alkyl  $\text{R}_1$  groups have up to 9 carbon atoms, most preferably  $\text{R}_1$  is a 2-ethylhexyl group; and  $\text{R}_{11}$  is a  $\text{C}_2\text{-C}_{14}$  alkyl, (poly) hydroxy alkyl, alkoxy or aralkyl group or a A or D unit as described above.

The anion  $\text{M}^-$  is a counterion for the cationically charged polyamine surfactant. Therefore, the number of  $\text{M}^-$  anions present will depend on the cationic charge of the polyamine surfactant, which depends on the groups A, B, C and D. The number of  $\text{M}^-$  anions will be at least 1. A preferred counterion is a halide anion, more preferably a sulphate anion.

The cationic polyamine surfactant is generally present in the composition or component thereof in an amount no greater than 60% by weight, preferably no greater than 10% by weight, most preferably in an amount no greater than 4.5% or even 3% by weight. The benefits of the invention are found even with very small amounts of the cationic polyamine surfactant of the invention. Generally there will be at least 0.01% by weight, preferably at least 0.05% or at least 0.1% by weight of the cationic surfactant in the detergent compositions of the invention.

#### Additional ingredients

The solid compositions or components thereof, comprise at least 0.1% by weight of additional ingredients. These ingredients can be selected from essentially all detergent ingredients known in the art and commonly used for solid laundry or dish washing detergents. The precise nature of these additional components, and levels of

incorporation thereof will depend on the physical form of the composition or component thereof, the specific performance and/ or benefits needed form the composition, and the precise nature of the washing operation for which it is to be used.

The cationic surfactant is in particularly useful in solid detergent compositions or components, which comprise additional ingredients which can cause dispensing, dispersion or dissolution problems and which thus may require a dispensing, dispersion or dissolution aid. Therefore, the cationic surfactant is particularly incorporated in in particularly solid compositions or components thereof, which comprise as additional ingredients anionically charged components such as anionic surfactants, such a sulfate and sulfonate surfactants, certain polymeric components, but also silicate builder materials and nonionic surfactants.

However, to further improve the dispensing and/ or dispersion and/ or dissolution of the solid compositions or components thereof, additional dispensing/ dispersion/ dissolution aids can be present, for example hydrotropes or effervescence systems, based on an acidity source and an alkalinity source capable of forming carbondioxide.

The compositions or components thereof, of the invention preferably contain one or more additional detergent components selected from additional surfactants, builders, sequestrants, bleach, bleach precursors, bleach catalysts, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, additional soil suspension and anti-redeposition agents soil releasing agents, perfumes and corrosion inhibitors.

#### Additional surfactant

The compositions or components thereof in accordance with the invention preferably contain an additional surfactant selected from anionic, nonionic, additional cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of

suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

#### Anionic surfactant

The detergent compositions or components of the preferably comprise an anionic surfactant. Any anionic surfactant useful for detergative purposes is suitable. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Particularly preferred compositions of the invention comprise both an alkyl sulfate surfactant and an sulfonate surfactant (preferably a linear alkylbenzene sulfonate), preferably in ratios of from 15:1 to 1:2, most preferably from 12:1 to 2:1.

Amounts of the one or mixtures of more than one anionic surfactant in the preferred composition may be from 1% to 50%, however, preferably anionic surfactant is present in amounts of from 5% to 40%, or even more preferred from 7% to 25% by weight of the composition. Preferred amounts of the alkyl sulfate surfactant are from 3% to 40%, or more preferably 6% to 30% by weight of the detergent composition. Preferred amounts of the sulfonate surfactant, preferably the alkyl benzene sulfonate surfactant in the detergent composition are from at least 1%, preferably at least 2%, or even at least 4% by weight. Preferred amounts of the alkyl benzene sulfonate surfactant are up to 23%, more preferably no greater than 20%, most preferably up to 15% or even 10%.

Other suitable anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

The performance benefits which result when an anionic surfactant is also used in the compositions of the invention are particularly useful for longer carbon chain length

anionic surfactants such as those having a carbon chain length of C<sub>12</sub> or greater, particularly of C<sub>14/15</sub> or even up to C<sub>16-18</sub> carbon chain lengths.

In preferred embodiments of the compositions of the invention there will be a significant excess of anionic surfactants, preferably a weight ratio of anionic to cationic surfactant of from 50:1 to 2:1, most preferably 30:1 to 8:1, or from 20:1 to 5:1. However, the benefits of the invention are also achieved where the ratio of cationic surfactant to anionic surfactant is substantially stoichiometric, for example from 3:2 to 4:3.

In a preferred embodiment of the invention the essential cationic is intimately mixed with one or more anionic surfactants prior to addition of the other detergent composition components to provide a readily soluble anionic/cationic complex. It may be useful to intimately mix substantially stoichiometric amounts of anionic and cationic surfactant prior to addition to any other detergent components, including any additional anionic surfactant.

#### Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use in the compositions or components of the invention include the primary and secondary alkyl sulfates, having a linear or branched alkyl or alkenyl moiety having from 9 to 22 carbon atoms or more preferably C<sub>12</sub> to C<sub>18</sub> alkyl; alkyl ethoxysulfates; fatty oleoyl glycerol sulfates; alkyl phenol ethylene oxide ether sulfates; the C<sub>5</sub>-C<sub>17</sub> acyl-N-(C<sub>1</sub>-C<sub>4</sub> alkyl) and -N-(C<sub>1</sub>-C<sub>2</sub> hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

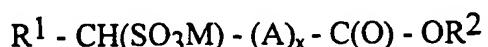
Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C<sub>9</sub>-C<sub>22</sub> alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C<sub>11</sub>-C<sub>18</sub>, most preferably C<sub>11</sub>-C<sub>15</sub> alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of a C<sub>5</sub>-C<sub>20</sub>, more preferably a C<sub>10</sub>-C<sub>16</sub>, more preferably a C<sub>11</sub>-C<sub>13</sub> (linear) alkylbenzene sulfonates, alkyl ester sulfonates, C<sub>6</sub>-C<sub>22</sub> primary or secondary alkane sulfonates, C<sub>6</sub>-C<sub>24</sub> olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

The alkyl ester sulfonated surfactant are preferably of the formula



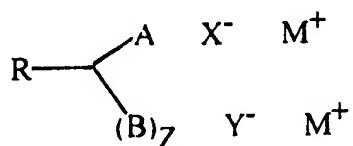
wherein R<sup>1</sup> is a C<sub>6</sub>-C<sub>22</sub> hydrocarbyl, R<sup>2</sup> is a C<sub>1</sub>-C<sub>6</sub> alkyl, A is a C<sub>6</sub>-C<sub>22</sub> alkylene, alkenylene, x is 0 or 1, and M is a cation. The counterion M is preferably sodium, potassium or ammonium.

The alkyl ester sulfonated surfactant is preferably a  $\alpha$ -sulpho alkyl ester of the formula above, whereby thus x is 0. Preferably, R<sup>1</sup> is an alkyl or alkenyl group of from 10 to 22, preferably 16 C atoms and x is preferably 0. R<sup>2</sup> is preferably ethyl or more preferably methyl.

It can be preferred that the R<sup>1</sup> of the ester is derived from unsaturated fatty acids, with preferably 1, 2 or 3 double bonds. It can also be preferred that R<sup>1</sup> of the ester is derived from a natural occurring fatty acid, preferably palmic acid or stearic acid or mixtures thereof.

Dianionic Surfactants

Dianionic surfactants are also suitable anionic surfactants for use in the compositions or components of the present invention. Preferred are the dianionic surfactants of the formula:

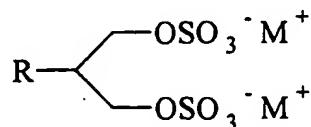


where R is an, optionally substituted, alkyl, alkenyl, aryl, alkaryl, ether, ester, amine or amide group of chain length C<sub>1</sub> to C<sub>28</sub>, preferably C<sub>3</sub> to C<sub>24</sub>, most preferably C<sub>8</sub> to C<sub>20</sub>, or hydrogen; A nad B are independently selected from alkylene, alkenylene, (poly) alkoxylene, hydroxyalkylene, arylalkylene or amido alkylene groups of chain length C<sub>1</sub> to C<sub>28</sub> preferably C<sub>1</sub> to C<sub>5</sub>, most preferably C<sub>1</sub> or C<sub>2</sub>, or a covalent bond, and preferably A and B in total contain at least 2 atoms; A, B, and R in total contain from 4 to about 31 carbon atoms; X and Y are anionic groups selected from the group comprising carboxylate, and preferably sulfate and sulfonate, z is 0 or preferably 1; and M is a cationic moiety, preferably a substituted or unsubstituted ammonium ion, or an alkali or alkaline earth metal ion.

The most preferred dianionic surfactant has the formula as above where R is an alkyl group of chain length from C<sub>10</sub> to C<sub>18</sub>, A and B are independently C<sub>1</sub> or C<sub>2</sub>, both X and Y are sulfate groups, and M is a potassium, ammonium, or a sodium ion.

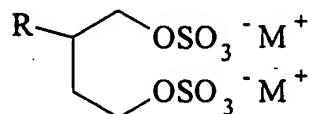
Preferred dianionic surfactants herein include:

(a) 3 disulphate compounds, preferably 1,3 C<sub>7</sub>-C<sub>23</sub> (i.e., the total number of carbons in the molecule) straight or branched chain alkyl or alkenyl disulphates, more preferably having the formula:



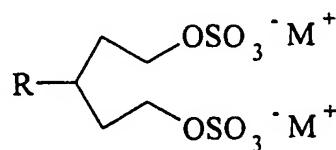
wherein R is a straight or branched chain alkyl or alkenyl group of chain length from about C<sub>4</sub> to about C<sub>20</sub>;

(b) 1,4 disulphate compounds, preferably 1,4 C<sub>8</sub>-C<sub>22</sub> straight or branched chain alkyl or alkenyl disulphates, more preferably having the formula:



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from about C<sub>4</sub> to about C<sub>18</sub>; preferred R are selected from octanyl, nonanyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and mixtures thereof; and

(c) 1,5 disulphate compounds, preferably 1,5 C9-C23 straight or branched chain alkyl or alkenyl disulphates, more preferably having the formula:



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from about C<sub>4</sub> to about C<sub>18</sub>.

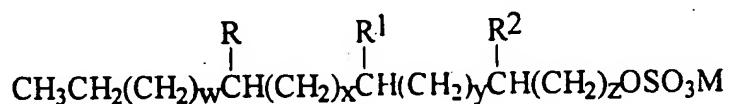
It can be preferred that the dianionic surfactants are alkoxylated dianionic surfactants.

The dianionic surfactant is typically present at levels of incorporation of from about 0.1% to about 20%, preferably from about 0.3% to about 15%, most preferably from about 0.5% to about 10% by weight of the detergent composition.

Mid-chain branched alkyl sulfates or sulphonates

Mid-chain branched alkyl sulfates or sulphonates are also suitable anionic surfactants for use in the compositions or components of the invention. Preferred are the mid-chain branched alkyl sulfates.

Preferred mid-chain branched primary alkyl sulfate surfactants are of the formula



These surfactants have a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom) which preferably comprises from 12 to 19 carbon atoms and their branched primary alkyl moieties comprise preferably a total of at least 14 and preferably no more than 20, carbon atoms. In compositions or components thereof of the invention comprising more than one of these sulfate surfactants, the average total number of carbon atoms for the branched primary alkyl moieties is preferably within the range of from greater than 14.5 to about 17.5. Thus, the surfactant system preferably comprises at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 12 carbon atoms or not more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and

further the average total number of carbon atoms for the branched primary alkyl moiety is within the range of greater than 14.5 to about 17.5.

Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl pentadecanol sulfate, 4-methyl pentadecanol sulfate, 5-methyl pentadecanol sulfate, 6-methyl pentadecanol sulfate, 7-methyl pentadecanol sulfate, 8-methyl pentadecanol sulfate, 9-methyl pentadecanol sulfate, 10-methyl pentadecanol sulfate, 11-methyl pentadecanol sulfate, 12-methyl pentadecanol sulfate, 13-methyl pentadecanol sulfate, 3-methyl hexadecanol sulfate, 4-methyl hexadecanol sulfate, 5-methyl hexadecanol sulfate, 6-methyl hexadecanol sulfate, 7-methyl hexadecanol sulfate, 8-methyl hexadecanol sulfate, 9-methyl hexadecanol sulfate, 10-methyl hexadecanol sulfate, 11-methyl hexadecanol sulfate, 12-methyl hexadecanol sulfate, 13-methyl hexadecanol sulfate, 14-methyl hexadecanol sulfate, and mixtures thereof.

Preferred di-methyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-methyl tetradecanol sulfate, 2,4-methyl tetradecanol sulfate, 2,5-methyl tetradecanol sulfate, 2,6-methyl tetradecanol sulfate, 2,7-methyl tetradecanol sulfate, 2,8-methyl tetradecanol sulfate, 2,9-methyl tetradecanol sulfate, 2,10-methyl tetradecanol sulfate, 2,11-methyl tetradecanol sulfate, 2,12-methyl tetradecanol sulfate, 2,3-methyl pentadecanol sulfate, 2,4-methyl pentadecanol sulfate, 2,5-methyl pentadecanol sulfate, 2,6-methyl pentadecanol sulfate, 2,7-methyl pentadecanol sulfate, 2,8-methyl pentadecanol sulfate, 2,9-methyl pentadecanol sulfate, 2,10-methyl pentadecanol sulfate, 2,11-methyl pentadecanol sulfate, 2,12-methyl pentadecanol sulfate, 2,13-methyl pentadecanol sulfate, and mixtures thereof.

#### Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula  $RO(CH_2CH_2O)_xCH_2COO^-M^+$  wherein R is a C<sub>6</sub> to C<sub>18</sub> alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula  $RO-(CHR_1-CHR_2-O)-R_3$  wherein R is

a C<sub>6</sub> to C<sub>18</sub> alkyl group, x is from 1 to 25, R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R<sub>3</sub> is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

#### Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R<sup>1</sup>)CH<sub>2</sub>COOM, wherein R is a C<sub>5</sub>-C<sub>17</sub> linear or branched alkyl or alkenyl group, R<sup>1</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

#### Alkoxylated nonionic surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

The nonionic surfactant is preferably present at a ratio to the anionic, if present, of from 10:1 to 1:10, more preferably from 5:1 to 1:10, even more preferably from 1:1 to 1:10.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

#### Nonionic alkoxylated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or

secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms, more preferably from 9 to 15 carbon atoms, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

#### Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R^2CONR^1Z$  wherein :  $R^1$  is H, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably C<sub>1</sub> alkyl (i.e., methyl); and  $R^2$  is a C<sub>5</sub>-C<sub>31</sub> hydrocarbyl, preferably straight-chain C<sub>5</sub>-C<sub>19</sub> alkyl or alkenyl, more preferably straight-chain C<sub>9</sub>-C<sub>17</sub> alkyl or alkenyl, most preferably straight-chain C<sub>11</sub>-C<sub>17</sub> alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycetyl.

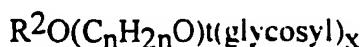
#### Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula:  $R^6CON(R^7)_2$  wherein  $R^6$  is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each  $R^7$  is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, and -(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>H, where x is in the range of from 1 to 3.

#### Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms;  $n$  is 2 or 3;  $t$  is from 0 to 10, and  $x$  is from 1.3 to 8. The glycosyl is preferably derived from glucose.

#### Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula  $R^3(OR^4)_xN^0(R^5)_2$  wherein  $R^3$  is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof;  $x$  is from 0 to 5, preferably from 0 to 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C<sub>10</sub>-C<sub>18</sub> alkyl dimethylamine oxide, and C<sub>10-18</sub> acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

#### Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions or components thereof in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula  $R(R')_2N^+R^2COO^-$  wherein  $R$  is a C<sub>6</sub>-C<sub>18</sub> hydrocarbyl group, each  $R^1$  is typically C<sub>1</sub>-C<sub>3</sub> alkyl, and  $R^2$  is a C<sub>1</sub>-C<sub>5</sub> hydrocarbyl group. Preferred betaines are C<sub>12-18</sub> dimethyl-ammonio hexanoate and the C<sub>10-18</sub> acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

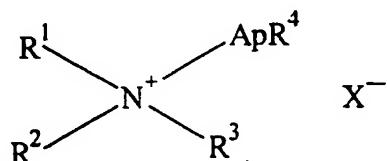
#### Additional Cationic surfactants

A suitable group of cationic surfactants which can be used in the

compositions or components thereof of the invention are cationic ester surfactants. The cationic ester surfactant is a compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group. Preferred cationic ester surfactants are water dispersible.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents Nos. 4228042, 4239660 and 4260529.

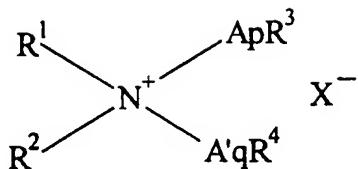
Other additional cationic surfactants are mono- or bis -alkoxylated amine surfactant. the mono-alkoxylated surfactants are of the general formula:



wherein R<sup>1</sup> is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 11 carbon atoms; R<sup>2</sup> and R<sup>3</sup> are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R<sup>4</sup> is selected from hydrogen (preferred), methyl and ethyl, X<sup>-</sup> is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C<sub>1</sub>-C<sub>4</sub> alkoxy, especially ethoxy (i.e., -CH<sub>2</sub>CH<sub>2</sub>O-), propoxy, butoxy and mixtures thereof; and p is from 1 to about 30, preferably 1 to about 15, most preferably 1 to about 8.

When used in granular detergent compositions cationic mono-alkoxylated amine surfactants wherein the hydrocarbyl substituent R<sup>1</sup> is C<sub>6</sub>-C<sub>11</sub>, especially C<sub>10</sub>, are preferred, because they enhance the rate of dissolution of laundry granules, especially under cold water conditions. as compared with the higher chain length materials.

Cationic bis-alkoxylated amine surfactants which are useful as additional cationic surfactants which have preferably the general formula:



wherein R<sup>1</sup> is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, more preferably 6 to about 11, most preferably from about 8 to about 10 carbon atoms; R<sup>2</sup> is an alkyl group containing from one to three carbon atoms, preferably methyl; R<sup>3</sup> and R<sup>4</sup> can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X<sup>-</sup> is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C<sub>1</sub>-C<sub>4</sub> alkoxy, especially ethoxy, (i.e., -CH<sub>2</sub>CH<sub>2</sub>O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

The levels of the cationic mono or bis--alkoxylated amine surfactants used in detergent compositions or components of the invention can range from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

#### Acid Source

In the solid compositions or components thereof, can comprise an acid source, such that the acid source is capable of reacting with an alkalinity system, in the presence of water to produce a gas.

The acid source is preferably present at a level of from 0.1% to 50%, more preferably from 0.5% to 25%, even more preferably from 1% to 12%, even more preferably from 1% to 7%, most preferably from 2% to 5% by weight of the composition. It can be preferred that the source of acidity is present in the range of about 1% to about 3%, most preferably about 3% by weight of the composition.

The acid source may be any suitable organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. The acid source may be a mono-, bi- or tri-protonic acid. Preferred derivatives include a salt or ester of the acid. The source of acidity is preferably non-hygroscopic, which can improve storage stability. However, a monohydrate acidic source can be useful herein. Organic acids and their

derivatives are preferred. The acid is preferably water-soluble. Suitable acids include citric, glutaric, tartaric acid, succinic or adipic acid, monosodium phosphate, sodium hydrogen sulfate, boric acid, or a salt or an ester thereof. Citric acid is especially preferred.

### Alkalinity

In the compositions or components of the present invention preferably an alkalinity system is present to achieve optimal cationic surfactant performance. The alkalinity system comprises components capable of providing alkalinity species in solution. Examples of alkalinity species include carbonate, bicarbonate, hydroxide, the various silicate anions, percarbonate, perborates, perphosphates, persulfate and persilicate. Such alkalinity species can be formed for example, when alkaline salts selected from alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate, including crystalline layered silicate, salts and percarbonate, perborates, perphosphates, persulfate and persilicate salts and any mixtures thereof are dissolved in water.

Examples of carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No.

2,321,001 published on November 15, 1973.

Suitable silicates include the water soluble sodium silicates with an  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of 2.0 is the most preferred silicate.

Preferred crystalline layered silicates for use herein have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or

4 and is preferably 2. The most preferred material is  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, available from Hoechst AG as NaSKS-6.

Water-soluble builder compound

The compositions or components in accordance with the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type, although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and

the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

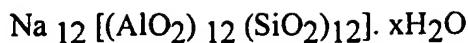
#### Partially soluble or insoluble builder compound

The compositions or components thereof, of the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula  $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$  wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$ .

Another preferred aluminosilicate zeolite is zeolite MAP builder. The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a  $d_{50}$  value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The  $d_{50}$  value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing  $d_{50}$  values are disclosed in EP 384070A.

#### Hydrotrope

Hydrotropes can be used in the solid detergent compositions or components thereof.

By the term hydrotrope when used herein is meant any of the hydrotropes known in the art, capable of reducing the viscosity of a mixture, comprising water and a surfactant component, in particular comprising a an anionic sulphonate surfactant. Among such hydrotropes there can be mentioned the short-chain (C<sub>1</sub>-C<sub>4</sub>) alk-aryl sulfonates. The water-soluble salts useful in the present invention include the alkali metal, alkaline earth metal, alkyl amine and ammonium salts of the sulfonic acid.

Preferred salts are sodium, potassium, and monoethanolamine sulfonate, and mixtures thereof.

In particular, the toluene sulfonates, the cumene sulfonates, the xylene sulfonates may be used in this invention. Most preferred is a sodium toluene sulfonate, being preferably a sodium toluene mono sulfonate.

The level of the hydrotrope is preferably from 0.01% to 25%, preferably from 0.1% to 15%, more preferably from 0.2% to 5%, even more preferably from 0.5% to 2%, most preferably from 0.8% to 1.8% by weight of the composition.

#### Heavy metal ion sequestrant

The compositions or components thereof in accordance with the present invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetraacetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali

metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The  $\beta$ -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

#### Organic peroxyacid bleaching system

A preferred feature of compositions or component thereof in accordance with the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

#### Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilise a coated form of the material which provides better storage stability for the perhydrate salt in the granular product and/or delayed release of the perhydrate salt on contact of the granular product with water. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}$ .

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to  $2\text{Na}_2\text{CO}_3\cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid.

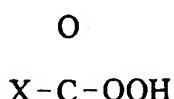
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

#### Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



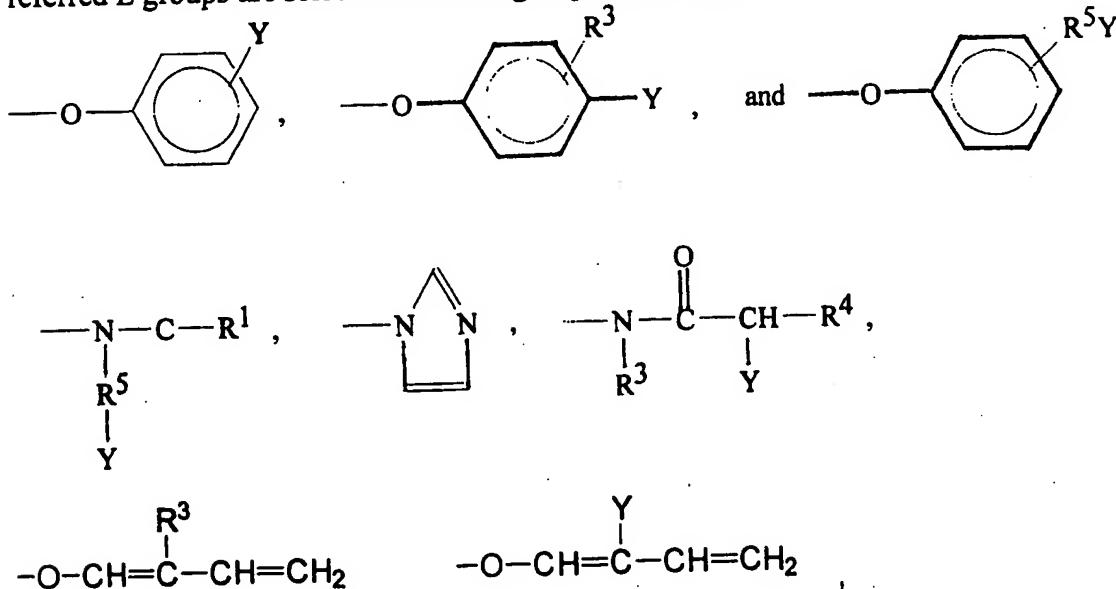
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

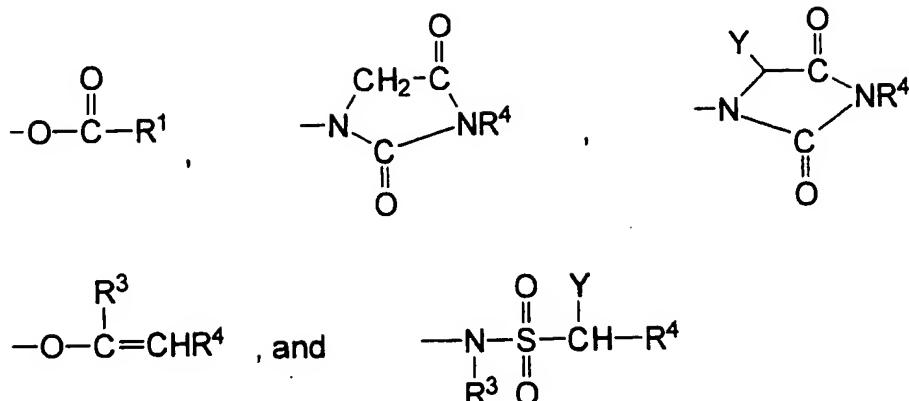
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

#### Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:





and mixtures thereof, wherein R<sup>1</sup> is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R<sup>3</sup> is an alkyl chain containing from 1 to 8 carbon atoms, R<sup>4</sup> is H or R<sup>3</sup>, R<sup>5</sup> is an alkenyl chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are -SO<sub>3</sub><sup>-</sup>M<sup>+</sup>, -CO<sub>2</sub><sup>-</sup>M<sup>+</sup>, -SO<sub>4</sub><sup>-</sup>M<sup>+</sup>, -N<sup>+</sup>(R<sup>3</sup>)<sub>4</sub>X<sup>-</sup> and O<--N(R<sup>3</sup>)<sub>3</sub> and most preferably -SO<sub>3</sub><sup>-</sup>M<sup>+</sup> and -CO<sub>2</sub><sup>-</sup>M<sup>+</sup> wherein R<sup>3</sup> is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

#### Alkyl percarboxylic acid bleach precursors

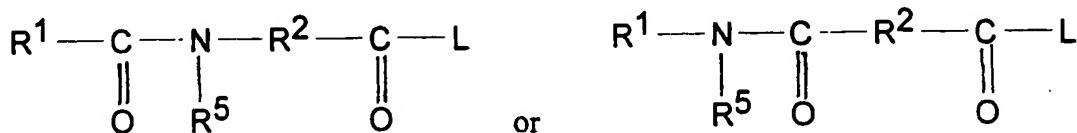
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N,N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein  $\text{R}^1$  is an alkyl group with from 1 to 14 carbon atoms,  $\text{R}^2$  is an alkylene group containing from 1 to 14 carbon atoms, and  $\text{R}^5$  is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically

present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

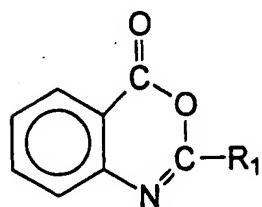
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

#### Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

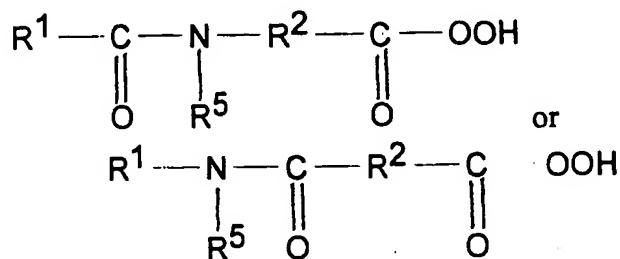


wherein R<sub>1</sub> is H, alkyl, alkaryl, aryl, or arylalkyl.

#### Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein  $\text{R}^1$  is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms.

Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

### Enzymes

The compositions or components thereof of the present invention may comprise one or more enzymes.

Preferred additional enzymatic materials include the commercially available enzymes. Said enzymes include enzymes selected from lipases, cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination of additional enzymes in a composition according to the present invention comprises a mixture of conventional applicable enzymes such as lipase, protease, amylase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes. Suitable enzymes are exemplified in US Patents 3,519,570 and 3,533,139.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Jnosh. et al. "Bleaching Compositions

Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

One or a mixture of proteolytic enzymes may be incorporated in the compositions of the present invention, generally at a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

If present in the detergent compositions of the present invention, the lipolytic enzyme component is generally present at levels of from 0.00005% to 2% of active enzyme by weight of the detergent composition, preferably 0.001% to 1% by weight, most preferably from 0.0002% to 0.05% by weight active enzyme in the detergent composition.

Suitable lipolytic enzymes for use in the present invention include those produced by micro-organisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1.372.034. Suitable lipases include those which show a positive immunological cross-section with the antibody of the lipase produced by the microorganism *Pseudomonas Hisorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other suitable commercial lipases include Amano-CHS. lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S.

Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases *ex* *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup> (Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever). The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use in the present invention.

Another preferred lipase for use in the present invention is D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa*. Most preferably the *Humicola lanuginosa* strain DSM 4106 is used.

By D96L lipolytic enzyme variant is meant the lipase variant as described in patent application WO 92/05249 in which the native lipase *ex* *Humicola lanuginosa* has the aspartic acid (D) residue at position 96 changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L. To determine the activity of the enzyme D96L the standard LU assay may be used (Analytical method, internal Novo Nordisk number AF 95/6-GB 1991.02.07). A substrate for D96L was prepared by emulsifying glycerine tributyrate (Merck) using gum-arabic as emulsifier. Lipase activity is assayed at pH 7 using pH stat. method.

The detergent compositions of the invention may also contain one or a mixture of more than one amylase enzyme ( $\alpha$  and/or  $\beta$ ). WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610;

EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial  $\alpha$ -amylases products are Purafect Ox Am<sup>®</sup> from Genencor and Termamyl<sup>®</sup>, Ban<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases :  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other preferred amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes if present are generally incorporated in the compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The detergent compositions of the invention may additionally incorporate one or more cellulase enzymes: Suitable cellulases include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, J61078384 and WO96/02653 which disclose fungal cellulases produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a

molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Peroxidase enzymes may also be incorporated into the detergent compositions of the invention. Peroxidases are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases, if present, are normally incorporated in the composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Said additional enzymes, when present, are normally incorporated in the composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The additional enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the compositions or components thereof of the present invention, and are preferably present as components of any particulate component of the detergent composition where they may act such as to bind the particulate component together. By organic polymeric compound is meant any polymeric organic compound commonly used as dispersants, anti-redeposition or soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Such an organic polymeric compound is generally incorporated in the compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylic acid or polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000. Polymaleates or polymaleic acid polymers and salts thereof are also suitable examples.

Polyamino compounds useful herein include those derived from aspartic acid including polyaspartic acid and such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, aspartic acid and vinyl alcohol or acetate, particularly those having an average molecular weight of from 1,000 to 30,000, preferably 3,000 to 10,000, are also suitable for incorporation into the compositions of the present invention.

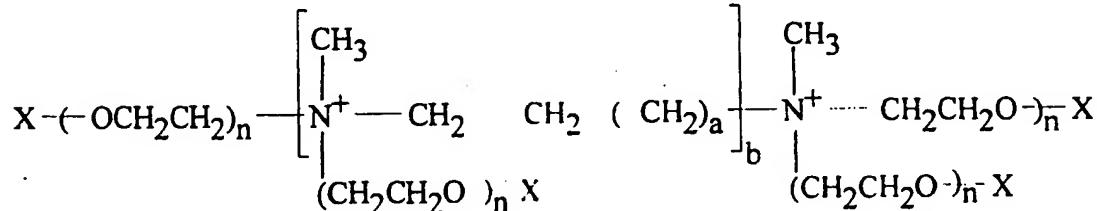
Other organic polymeric compounds suitable for incorporation in the detergent compositions of the present invention include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose, ethylhydroxyethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000 to 10000, more particularly 2000 to 8000 and most preferably about 4000.

Cationic soil removal/anti-redeposition compounds

The composition or components thereof of the invention may comprise water-soluble cationic ethoxylated amine compounds with particulate soil/clay-soil removal and/or anti-redeposition properties. These cationic compounds are described in more detail in EP-B-111965, US 4659802 and US 4664848.

Particularly preferred of these cationic compounds are ethoxylated cationic monoamines, diamines or triamines. Especially preferred are the ethoxylated cationic monoamines, diamines and triamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 2, 1 or 0; for cationic monoamines (b=0), n is preferably at least 16, with a typical range of from 20 to 35; for cationic diamines or triamines, n is preferably at least about 12 with a typical range of from about 12 to about 42.

These compounds where present in the composition, are generally present in an amount of from 0.01 to 30% by weight, preferably 0.05 to 10% by weight.

### Suds suppressing system

The compositions of the invention are preferably substantially free of any suds suppressing agents where high foaming is desired. It can be preferred that the composition require low-sudsing, and that thus incorporation of suds suppressant for foam control are desirable. They are preferably present in amounts no greater than 2.5% and most preferably in amounts no greater than 1.5% or even no greater than 0.5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alkanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products

of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

- (a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination
  - (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and
  - (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;
- (b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;
- (c) an inert carrier fluid compound, most preferably comprising a C<sub>16</sub>-C<sub>18</sub> ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is

a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

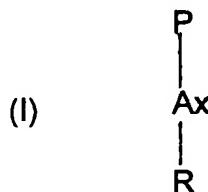
Polymeric dye transfer inhibiting agents

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

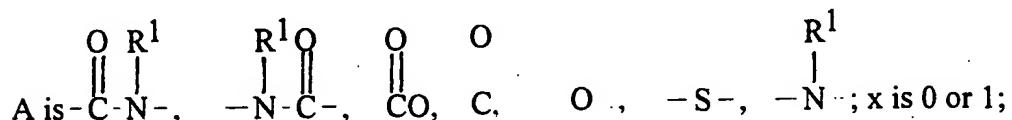
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

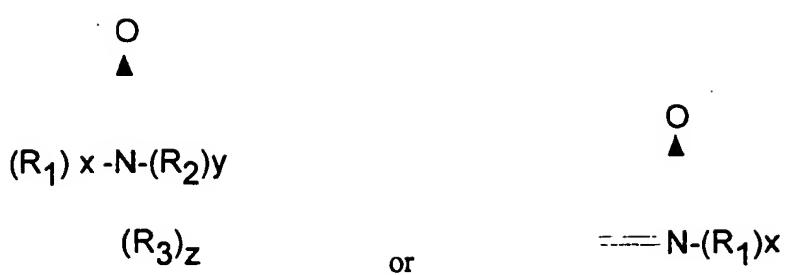


wherein P is a polymerisable unit, and



R<sup>1</sup> is H or C<sub>1-6</sub> linear or branched alkyl; or may form a heterocyclic group with R; R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, N-substituted pyrrole, imidazole, N-substituted pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, N-substituted pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

**b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole**

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having a preferred average molecular weight range of from 5,000 to 100,000, or 5,000 to

50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Corporation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

The compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

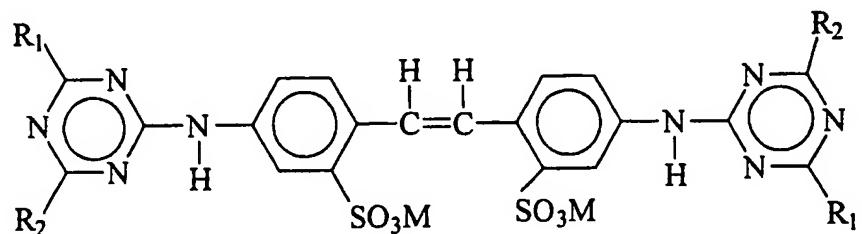
e) Polyvinylimidazole

The compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R<sub>1</sub> is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R<sub>2</sub> is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R<sub>1</sub> is anilino, R<sub>2</sub> is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R<sub>1</sub> is anilino, R<sub>2</sub> is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R<sub>1</sub> is anilino, R<sub>2</sub> is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

### Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present compositions or components. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric or polymeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

#### Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

#### pH of detergent formulation

While the detergent compositions of the present invention are operative within a wide range of wash pHs (e.g. from about 5 to about 12), they are particularly suitable when formulated to provide a near neutral wash pH, i.e. an initial pH of from about 7.0 to about 10.5 at a concentration of from about 0.1 to about 2% by weight in water at 20°C, whereby it can be beneficial for an optimum performance of the cationic surfactants present in the compositions of the invention that the pH is adjusted to be above 7.0, i.e. more alkaline. In such formulations, the wash pH is preferably from about 8.0 to about 10.5, most preferably from 8.0 to 9.0.

#### Form of the compositions

The solid compositions in accordance with the invention can take a variety of physical forms including granular, tablet, flake or pastille forms. The compositions may be pre-treatment compositions or may be conventional washing detergents. The compositions are preferably compacted, particularly the so-called concentrated granular detergent compositions.

The benefits of the invention are in particular found for granular compositions which have a bulk density of at least 570g/l, or even at least 680g/l..

The granular detergent compositions or components thereof in accordance with the present invention can be made via a variety of methods, including spray-drying, dry-mixing, extrusion, agglomerating and granulation. The cationic surfactant can be added to the other detergent components by mixing, agglomeration (preferably combined with a carrier material), granulation or as a spray-dried component.

The compositions in accordance with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach.

In one aspect of the invention the mean particle size of the components of granular compositions in accordance with the invention, should preferably be such that no more than 15% of the particles or components are greater than 1.8mm in diameter and not more than 15% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10% to 50% of the particles has a particle size of from 0.2mm to 0.7mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

In a further aspect of the invention at least 80%, preferably at least 90% by weight of the composition comprises particles of mean particle size at least 0.8 mm, more preferably at least 1.0 mm and most preferably from 1.0, or 1.5 to 2.5 mm. Most preferably at least 95% of the particles will have such a mean particle size. Such particles are preferably prepared by an extrusion process.

Compacted solids, which are not in a granular form, may be manufactured using any suitable compacting process, such as tabletting, briquetting or extrusion, preferably tabletting. Preferably tablets for use in dish washing processes, are manufactured using a standard rotary tabletting press using compression forces of from 5 to 13 KN/cm<sup>2</sup>, more preferably from 5 to 11KN/cm<sup>2</sup> so that the compacted solid has a

minimum hardness of 176N to 275N, preferably from 195N to 245N, measured by a C100 hardness test as supplied by I. Holland instruments. This process may be used to prepare homogeneous or layered tablets of any size or shape. Preferably tablets are symmetrical to ensure the uniform dissolution of the tablet in the wash solution.

#### Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Dosage is dependent upon the particular conditions such as water hardness and degree of soiling of the soiled laundry.

The detergent composition may be dispensed for example, from the drawer dispenser of a washing machine or may be sprinkled over the soiled laundry placed in the machine.

In one use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

#### Machine dishwashing method

Any suitable methods for machine dishwashing or cleaning soiled tableware, particularly soiled silverware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing composition in accord with the invention. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

#### Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

#### Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C <sub>11</sub> -13 alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
CxyAS	:	Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate
C46SAS	:	Sodium C <sub>14</sub> - C <sub>16</sub> secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	:	C <sub>1x</sub> -C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
PAS	:	Salt of R <sub>1</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> R <sub>2</sub> , wherein R <sub>1</sub> is C <sub>2</sub> -C <sub>3</sub> hydroxyalkyl and R <sub>2</sub> is primary ethylene amine or primary propylene amine

PAS <sub>1</sub>	:	Salt of R <sub>1</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> R <sub>2</sub> wherein R <sub>1</sub> is C <sub>5</sub> -C <sub>8</sub> alkyl and R <sub>2</sub> is primary ethylene amine or primary propylene amine
PAS <sub>2</sub>	:	Salt of 2-ethylhexyl, methyl, hydroxethyl-ammonium di(C <sub>1</sub> -C <sub>4</sub> alkyl) ethylene amine
PAS <sub>3</sub>	:	Salt of 2-ethylhexyl, methyl, hydroxethyl-ammonium di (C <sub>1</sub> -C <sub>4</sub> alkyl) propylene amine
QAS	:	R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> - C <sub>14</sub>
QAS 1	:	R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub> - C <sub>11</sub>
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	:	Sodium toluene sulphonate
CFAA	:	C <sub>12</sub> -C <sub>14</sub> (coco) alkyl N-methyl glucamide
TFAA	:	C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide
TPKFA	:	C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate
Zeolite A	:	Hydrated sodium aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> .27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6	:	Crystalline layered silicate of formula δ- Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
Citric acid	:	Anhydrous citric acid
Citric acid 1	:	Crystalline citric acid
Borate	:	Sodium borate
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 2.0:1)
Sulfate	:	Anhydrous sodium sulfate
Mg sulfate	:	Anhydrous magnesium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000

AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
NAC-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate

TAED	:	Tetraacetyl ethylenediamine
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
Photoactivated	:	Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer
Photoactivated	:	Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
HEDP	:	1,1-hydroxyethane diphosphonic acid
PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000
PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
QEA	:	bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> )(CH <sub>3</sub> ) -N <sup>+</sup> -C <sub>6</sub> H <sub>12</sub> -N <sup>+</sup> (CH <sub>3</sub> ) bis((C <sub>2</sub> H <sub>5</sub> O)-(C <sub>2</sub> H <sub>4</sub> O)) <sub>n</sub> , wherein n = from 20 to 30
SRP 1	:	Anionically end capped poly esters
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer

PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Wax	:	Paraffin wax

In the following examples all levels are quoted as % by weight of the composition:

**Example 1**

The following high density granular laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
STS	0.5	-	-	-	0.5	1.0
PAS	3.0	1.0	0.5	-	-	1.4

PAS <sub>1</sub>	-	-	-	2.0	7.0	0.3
QAS	-	0.8	-	-	-	-
QAS (I)	-	-	-	-	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric acid	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0
SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Citric acid	1.0	-	2.0	-	-	1.0
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NAC-OBS	-	2.0	1.0	-	-	-

DTPMP	0.25	0.25	0.25	0.25	-	-
SRP I	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Protease I	-	-	0.26	1.0	-	-
Protease	0.26	0.26	-	-	1.5	1.0
Cellulase	0.3	-	-	0.3	0.3	0.3
Amylase	0.1	0.1	0.1	0.4	0.5	0.5
Lipase (1)	0.3	-	-	0.5	0.5	0.5
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	-	20 ppm	20 ppm
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume	0.3	0.3	0.3	0.4	0.4	0.4
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
Misc/minors to 100%						

Density in g/litre	850	850	850	850	850	850
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**Example 2**

The following granular laundry detergent compositions G to L of particular utility under European machine wash conditions were prepared in accord with the invention:

	G	H	I	J	K	L
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
STS	1.0	-	-	-	1.0	-
QAS	0.8	-	-	-	-	-
QAS II	-	-	-	-	-	0.7
PAS	1.0	1.5	0.7	0.3	-	-
PAS <sub>1</sub>	-	-	-	0.3	1.0	3.8
STPP	19.7	-	-	-	-	-

Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6/silicate	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Citric acid	3.0	1.0	-	0.5	1.0	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2

HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (1) (ppm)	15 ppm	27 ppm	-	-	20 ppm	20 ppm
Photoactivated bleach (2) (ppm)	15 ppm	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0

Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	M	N	O	P
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0

PAS	0.5	-	-	1.5
PAS <sub>1</sub>	-	1.0	4.0	-
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
Misc/minor to 100%				

#### Example 4

The following granular detergent formulations were prepared in accord with the invention.

	Q	R	S	T	U	V
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3

Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
PAS	3.0	0.6	-	-	0.4	-
PAS <sub>1</sub>	-	-	2.0	1.0	0.4	0.3
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-

Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

### Example 5

The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
PAS <sub>2</sub>	0.4	0.9	-
PAS <sub>3</sub>	-	-	2.0
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
PAS <sub>1</sub>	2.0	-	-
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	9.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5

Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

### Example 6

The following granular detergent formulations were prepared in accord with the invention.

	Z	AA	BB	CC
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
PAS	2.0	7.0	-	-
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1

Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PAS <sub>1</sub>	-	-	0.9	1.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
Sud suppressor	-	0.5	0.5	-
Misc/minor to 100%				

Example 7

The following granular detergent compositions were prepared in accord with the invention.

	DD	EE	FF
Blown powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-

PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS (I)	-	-	1.0
PAS	1.0	1.5	1.0
PAS <sub>1</sub>	0.5	-	-
Photoactivated bleach	15 ppm	15 ppm	15 ppm
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			
Density (g/litre)	700	700	700

### Example 8

The following detergent compositions, according to the present invention were prepared:

	GG	HH	II
<b>Blown Powder</b>			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
<b>Agglomerates</b>			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
PAS <sub>1</sub>	-	0.7	0.5
Carbonate	8.0	8.0	4.0
<b>Spray On</b>			
Perfume	0.3	0.3	0.3

C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
PAS	1.8	-	1.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

### Example 9

The following detergent formulations, according to the present invention were prepared:

	JJ	KK	LL	MM
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	-
TFAA	-	1.0	-	-
PAS	1.0	-	2.0	-
PAS <sub>1</sub>	-	1.0	-	0.5
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-

DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sodium sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
Perfume	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

### Example 10

The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AD	AE	AF	AG	AH	AI	AJ	AK
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-

Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	0.1	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.10	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0
PAS <sub>1</sub>	0.7	1.0	1.0	3.0	1.5	0.5	-	-
PAS	-	-	-	-	-	0.5	2.8	1.0

### Example 11

The following laundry detergent compositions are in accord with the invention:

	AL	AM	AN	AO
C45 AS	8	10	11	4
C45E1S	4	3	-	1
LAS	8	14	-	4
C16 SAS	-	-	3	-
PAS	5.0	0.5	0.7	1.0
MES	-	-	12	-
PAS/PAS <sub>1</sub>	1.0	3.0	1.0	1.0
C23E6.5	1.5	1.5	1.5	1.5
Zeolite A	17.8	20.8	20.8	27.8
AA	2.3	2.3	2.3	2.3
Carbonate	27.3	27.3	27.3	27.3
Silicate	0.6	0.6	0.6	0.6
Perborate	1.0	1.0	1.0	1.0
Protease	0.3	0.3	0.3	0.3

Cellulase	0.3	0.3	0.3	0.3
SRP1	0.4	0.4	0.4	0.4
Brightener	0.2	0.2	0.2	0.2
PEG	1.6	1.6	1.6	1.6
PB1	16.0	6.0	-	-
NOBS	2.4	4.5	0.8	3.5
PC	-	-	8.0	15.0
Sulfate	5.5	5.5	5.5	5.5
Silicone Antifoam	0.42	0.42	0.42	0.42
TAED	0.5	4.5	8.0	2.0
Moisture & Minors	---Balance---			
Density (g/L)	660	660	660	660

### Example 12

The following laundry detergent compositions are in accord with the invention:

	AP	AQ	AR	AS	AT
C45 AS	5	7	6	4	12
C45 E3S	2	-	4	-	5
LAS	14	8	-	18	5
PAS/PAS <sub>1</sub>	0.5	1.5	1.0	4.0	0.8
C16 SAS	-	-	1	-	1
MES	-	-	10	-	-
TFAA	1.6	-	-	-	-
C24E3	4.9	4.9	4.9	4.9	4.9
Zeolite A	15	15	15	15	15
QAS	1.0	-	-	-	1.0
NaSKS-6	11	11	11	11	11
Citrate/citric	1.0	2.0	3	3	-
MA/AA	4.8	4.8	4.8	4.8	4.8
HEDP	0.5	0.5	0.5	0.5	0.5
Carbonate	8.5	8.5	8.5	8.5	8.5
Protease	0.9	0.9	0.9	0.9	0.9
Lipase	0.15	0.15	0.15	0.15	0.15

Cellulase	0.26	0.26	0.26	0.26	0.26
Amylase	0.36	0.36	0.36	0.36	0.36
NOBS	-	-	-	4.0	5.0
NACA-OBS	4.0	2.0	6.0	-	-
TAED	4.0	-	2.0	1.0	0.5
PB1	-	-	14.0	-	8.0
Percarbonate	20.0	14.0	-	22.0	-
SRP1	0.2	0.2	0.2	0.2	0.2
QEA1	1.0	1.5	-	-	-
Brightener	0.2	0.2	0.2	0.2	0.2
Sulfate	2.3	2.3	2.3	2.3	2.3
Silicone Antifoam	0.4	0.4	0.4	0.4	0.4
Moisture & Minors	---Balance---				
Density (g/L)	850	850	850	850	850

### Example 13

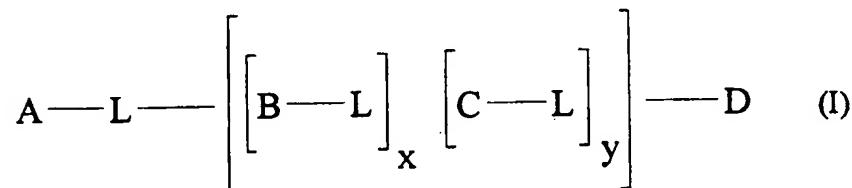
The following laundry detergent compositions AU to AZ are in accord with the invention:

	AU	AV	AW	AX	AY	AZ
C45 AS	5	-	6	12	2	-
C45E1S	1	-	-	1	5	2
MBAS 16.5, 1.7	32	-	-	16	-	8
LAS	-	20	8	23	12	16
C16 SAS	1	4	-	-	-	-
MES	14	-	-	-	-	-
PAS/PAS <sub>1</sub>	1.0	4.0	0.7	1.0	1.5	1.2
C23E6.5	3.6	3.6	3.6	3.6	3.6	3.6
PAS/PAS <sub>1</sub>	2.0	1.0	0.5	5.5	0.8	1.0
QAS	-	0.5	-	-	0.5	-
Zeolite A	9.0	9.0	9.0	9.0	9.0	9.0
Polycarboxylate	7.0	7.0	7.0	7.0	7.0	7.0
Carbonate	18.4	18.4	18.4	18.4	18.4	18.4
Silicate	11.3	11.3	11.3	11.3	11.3	11.3

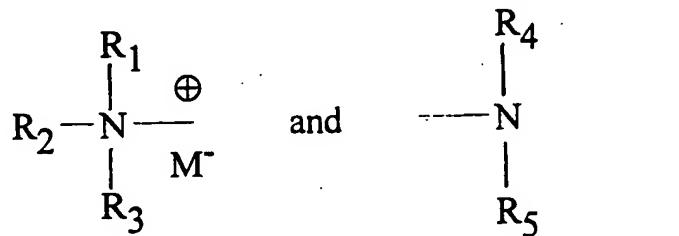
PB1	-	-	3.9	10.0	3.9	15.0
TAED	2.0	5.0	-	-	6.0	2.0
Percarbonate	7.0	7.0	-	-	-	-
NOBS/DDOBS	4.1	4.1	4.1	4.1	-	4.1
Protease	0.9	0.9	0.9	0.9	0.9	0.9
SRP1	0.5	0.5	0.5	0.5	0.5	0.5
Brightener	0.3	0.3	0.3	0.3	0.3	0.3
PEG	0.2	0.2	0.2	0.2	0.2	0.2
Sulfate	5.1	5.1	5.1	5.1	5.1	5.1
Silicone Antifoam	0.2	0.2	0.2	0.2	0.2	0.2
Moistures & Minors	---Balance---					
Density (g/L)	810	810	810	810	810	810

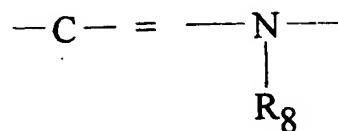
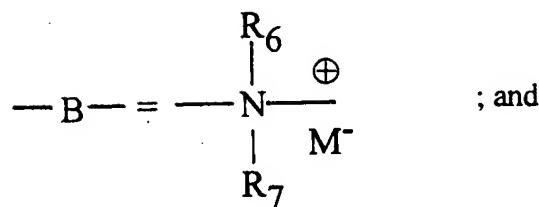
What is claimed is:

1. A solid detergent composition or component comprising:
  - (a) at least 0.01% by weight of the composition or the component thereof, one or more cationic surfactants, comprising at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group.
  - (b) from 0.1% to 99.99% by weight of the composition or the component thereof, additional detergent ingredients.
2. A composition or component according to claim 1 wherein the cationic surfactant is a polyamine cationic surfactant of the general formula:



wherein L is a linking unit, and each L is independently selected from the group consisting of C<sub>2</sub>-C<sub>30</sub> linear or branched alkylene, alkenylene, alkarylene, aralkylene, arylene, (poly) hydroxyalkylene, (poly) alkylenoxy, (poly) hydroxy alkenylene; L can be substituted by one or more A, B, C or D units; x is a number from 0 to 10, y is a number from 0 to 10; and wherein the units A- and D- are each independently selected from





wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are independently selected from the group consisting of C<sub>1</sub>-C<sub>30</sub> linear or branched alkyl, alkenyl, alkaryl, aralkyl, aryl, (poly) hydroxyalkyl, (poly) hydroxy alkenyl, alkoxy group and hydrogen, one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> or R<sub>8</sub> can be a linear or branched polyoxyalkylene group with from 2 to 26 oxyalkylene units or R<sub>1</sub> and R<sub>2</sub>, R<sub>1</sub> and R<sub>2</sub> and R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> or R<sub>6</sub> and R<sub>7</sub> form together with the nitrogen atom part of a ring structure; or R<sub>3</sub> is not present and R<sub>1</sub> or R<sub>2</sub> is double bonded to the nitrogen; or R<sub>7</sub> is not present and R<sub>6</sub> is double bonded to the nitrogen; or R<sub>5</sub> is not present and R<sub>4</sub> is double bonded to the nitrogen; or, when x and y are 0, R<sub>1</sub> or R<sub>2</sub> or R<sub>3</sub> and R<sub>4</sub> or R<sub>5</sub> form together with the nitrogen atoms of A and D part of a ring structure; M<sup>+</sup> is one or more counterions, and at least one A or D comprises a quaternized ammonium group in which none of R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> is hydrogen, or at least one B is present in which neither R<sub>6</sub> nor R<sub>7</sub> is hydrogen, and at least one A or D comprises a primary, secondary or tertiary amine group, or at least one C is present.

3. A composition or component according to claim 2 comprising a polyamine cationic surfactant wherein x=0 and y=0.
4. A composition or component according to claim 2 or 3 comprising a polyamine cationic surfactant wherein R<sub>4</sub> and R<sub>5</sub> are, independently from each other, C<sub>1</sub>-C<sub>6</sub> alkyl or (poly) hydroxyalkyl group or hydrogen atom.
5. A composition or component according to any of claims 2 to 4 comprising a polyamine cationic surfactant, wherein L is a C<sub>2</sub>-C<sub>4</sub> linear or branched alkyl or hydroxyalkyl group.

6. A composition according to any preceding claim in which the cationic surfactant is present in an amount of from 0.01% to 20% by weight, preferably of from 0.05% to 5% by weight of the composition.
7. A composition or component thereof according to any preceding claim in which the anionic surfactant is selected from linear or branched C9-C22, preferably C<sub>16-18</sub>, alkyl sulfate surfactants or alkoxylated alkyl sulfates and C<sub>10-20</sub>, preferably C<sub>11-13</sub> alkyl benzene sulfonate surfactants.
8. A composition or component thereof according to any preceding claim, having a bulk density of at least 570 g/l, preferably at least 680 g/l.
9. A composition or component thereof according to any preceding claim, comprising an effervescence system comprising an acidity source and an alkalinity source, capable of forming carbon dioxide upon contact with water.
10. A composition or component thereof according to any preceding claim, comprising a nonionic surfactant, preferably selected from group consisting of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.
11. A composition according to any preceding claim, comprising an agglomerated component which comprises the cationic surfactant.
12. A composition according to any of claims 1 to 10, comprising an spray-dried component which comprises the cationic surfactant.
13. The use of at least 0.01%, preferably at least 0.05% by weight of one or more cationic surfactants, comprising at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group, in a solid detergent composition for improving the dispensing and/ or dispersion of the composition into the wash water.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/02367

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 1/40, 1/42, 1/44, 1/48, 1/62

US CL :510/504, 506

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/504, 506

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN structure search

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US H1313 (JOHNSON et al.) 03 May 1994, column 3, line22-column 5, line 33; column 7, line 22-column 8, line 10; column 14, line 36-column 15, line 22.	1-4, 13
X	US 4,248,827 (KITKO) 03 February 1981, column 3, line 34-column 5, line 15; column 10, line 52-column 11, line 35.	1-4, 13
A	US 4,960,526 (PUENTES-BRAVO et al.) 02 October 1990, entire document.	
A	JP 06-123,071 (KAO CORP) 06 May 1994, entire document.	
A	JP 01-113,500 (DAINICHISEIKA LTD.) 02 May 1989, entire document.	

 Further documents are listed in the continuation of Box C. See patent family annex.

•	Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
•A•	document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
•B•	earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
•L•	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
•O•	document referring to an oral disclosure, use, exhibition or other means		
•P•	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

24 MARCH 1998

Date of mailing of the international search report

23 APR 1998

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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US98/02367**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 5-12 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.